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Analysis of hydrocarbons in bitumens from raised bog profiles

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Abstract: **The purpose of this paper is to study the composition of the hydrocarbons found in peat bitumen. As an object of the study two peat profiles from ombrotrophic bogs were used. Efficiency of different solvents was studied and considering the yield of obtained bitumen as most effective can be considered chlorinated hydrocarbons. The concentration of peat bitumen clearly reflects the decomposition degree of the original living material and presence of remains of terrestrial biota. The amounts of bitumen in the studied samples range from 1.8 till 8.1 %.**

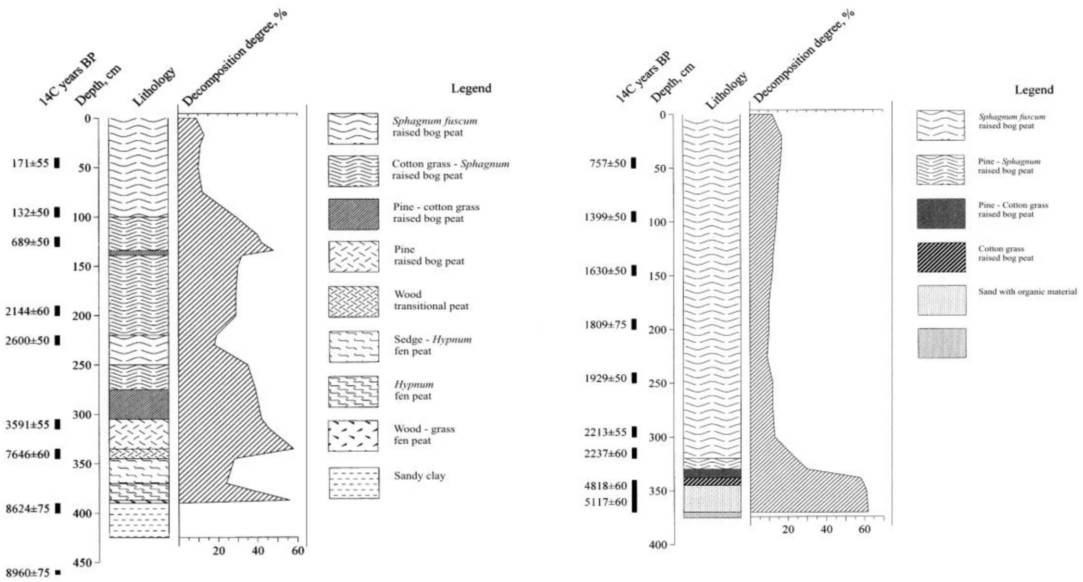
The clean-up procedure of the obtained samples, which was carried out by using solid phase extraction cartridges, ensured removal of more hydrophilic ingredients from the peat bitumens and isolation of hydrocarbon ingredients. The studied bitumen contains linear and cyclic hydrocarbons in the range from C_{12} till C_{27}.

Keywords: **peat, bitumen, hydrocarbons, GC-MS**

I. Introduction

Peat consists of remains of wetland (bog) plants, transformation products of living organic matter – humic substances) and many groups of organic substances originating both from living organisms, both during their decay process in very specific conditions of bog environment. Of importance amongst other groups of peat ingredients are highly hydrophobic substances called as peat waxes and bitumen. Bitumen is peat component which dissolves in hot organic solvents and contain peat waxes – a mixture of esters, acids, alcohols and peat hydrocarbons [1]. For extraction of peat bitumen many solvents have been suggested, including hydrocarbons, chlorinated hydrocarbons, technical solvents (petroleum ether, gasoline and others), ethers (diethyl ether, 1,4-dioxan), esters (ethyl acetate and other), various alcohols as well as such solvents as carbon disulfide [2].

The bitumen content in different peats ranges from 1 % to as much as 13% [2] and is very much influenced by the peat type. Moreover, the composition of peat bitumen is very much influenced by the processes of their genesis and significant differences have been found between the peats from low-moor, high-moor and transitional peats [3]. Peat bitumen has been an object of many studies also considering industrial application possibilities [2-5], however significant part of the studies were done more than 20 – 30 years ago, before the start of large-scale production of polymers replacing peat and other bitumens [2]. Nowadays there are many replacements of the former areas of use of peat bitumen and from the perspective of large scale production their importance is relatively minor.



A B

Fig.1. Peat stratigraphy and peat decomposition degree in Eipurs (A) and in Dzelves (B) bogs

At the same time, there is both theoretical and applied interest to study peat bitumen in modern times. The composition and amount of peat bitumen might reveal the peat genesis process and transformation of living organic matter during humification reactions. Peat bitumen composition may reveal the processes common during formation of fossil carbon containing deposits [6]. Another important and prospective object of peat bitumen study includes possibly biologically active substances in the peat bitumen such as sterols [7], influencing biological activity of peats and their bitumen. The number of recent studies dedicated to analysis of peat bitumen is relatively low [1, 8] but such methods as GC-MS and HPLC-MS have not been much used to identify peat bitumen composition [3].

The group of substances of particular interest amongst the peat bitumen ingredients is hydrocarbons. Presence and composition of hydrocarbons in peat bitumen has been analysed only in few studies [3-6] and significant dependence on the peat decomposition processes has been stated. It has been suggested that the major source of hydrocarbons in peat bitumen can be the decomposition reactions of waxes, present in living plants, microbial metabolites of microorganisms, decomposing bog vegetation and transformation reactions of living organic material [7]. Thus, further studies of hydrocarbons present in peat bitumen could be of definite importance.

The aim of this study is to analyse peat bitumen content in well characterized ombrotrophic bog peat profile and examine the hydrocarbon composition of peat bitumen

II. Materials and methods

Peat profiles were obtained from [9, 10] ombrotrophic bogs Eipurs and Dzelve. Both bogs are located in lowlands, they are of similar origin (they developed due to ground paludification), but they have differing very much different lithology (Figure 1). Both bogs are typical raised bogs and neither presently, nor historically have been affected by direct pollution sources.

Coring, sounding and sampling have been accomplished in the central areas of both mires, where the most complete geological section is present and which was least affected by the processes at adjacent areas. The 0.5 m long peat monolithic samples were placed in special plastic cartridges and wrapped in polyethylene film to preserve natural moisture and other parameters.

Samples were brought to the lab and sliced into 0.10 m sections using a stainless steel knife. The outside edges of each 0.05 m sample were discarded, because of probable contamination during sampling.

Samples were dried at room temperature and by using lyophilization to avoid loss of hydrocarbons.

Peat decomposition analysis. Peat decomposition degree was estimated according to Standard GOST 10650-72. The method includes wet sieve analysis to remove coagulated humus from fiber, centrifugation of samples and determination of decomposition degree.

Peat botanical composition. Peat botanical composition is closely related to plant nutrition conditions, bog characteristics, relief, underlying deposits and groundwater mineralization degree, which substantially affect peat decomposition degree, moisture and properties [11].

The analysis of botanical composition was performed using Carl-Zeiss binocular microscope, while the decomposition degree [12] was determined by using known methods. Peat type and H-value were examined in the field and later adjusted in the laboratory.

Analysis of peat properties. The ^{14}C dating was done at the Institute of Geology of Tallinn Technical University (Estonia). Carbon, hydrogen, nitrogen and sulphur concentrations in peat samples (elemental analysis of C, H, N, S) was carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments) by combustion-gas chromatography technique. The instrument was calibrated using cystine (Sigma – Aldrich Inc.) and all peat samples were analyzed in duplicate. Ash content was measured after heating 50 mg of each peat sample at 750 ^{0}C for 8 h. Elemental composition was corrected considering the ash content, and the oxygen amount was calculated as a difference.

Humification degree. 1.00 g of peat sample was treated for 1.5 hrs with 25 ml of 8 % NaOH in 25 ml plastic tubes in a boiling water bath (95 ºC) and filtered. 12.5 ml of the filtrate were diluted to 100 ml and absorption was measured at 540 nm. The peat humification degree was expressed as absorption at 540 nm.

Extraction of bitumen. 10 g of dried and milled peat were extracted for 6 hrs with dichloromethane in Soxlet extractor. The extract was evaporated under reduced pressure and finally dried in vacuum.

Clean-up of bitumen for hydrocarbon analysis. 100 mg of crude peat bitumen were dissolved into 10 ml of dichloromethane and applied to C_{18} cartridge, equilibrated with 5 ml dichloromethane. The cartridge was eluted with 20 ml of hexane and the eluted samples were evaporated in a rotavapor to about 1 ml at 40 ^oC .

Gas chromatography – mass spectrometry. GC-2010 (Shimadzu) quadrupole analyser QP-2010 with an autoinjector AOC-20i (Shimadzu) with a column Rtx-1ms (30m × 0.25 mm × 0.25 μm was used. The following instrumental parameters were applied: injection volume: 1 μl, temperature program from 60 ˚C (1 min) till 300 ˚C with 10 ˚C/min. Injector: flow split 1:2, t=300 ˚C, carrier gas: He (5.0), flow 1.01 ml/min. Mass spectrometer operated at 70 eV, with a mass range of m/z 40 - 350 , SCAN regime.

Data treatment. Statistical analyses were performed using SPSS 16 Software. The fitting of the obtained data to the normal distribution was checked with the Kolmogorov-Smirnov tests. In further analysis non-parametric methods were used. Relationships between different characteristics were assessed by Spearman rank correlation coefficients. In all cases the significance level was p=0.05.

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III. Results and Discussion

The aim of this study is to analyze the relations between the variability of peat properties, its humification degree and content and composition of peat bitumen hydrocarbons on the example of analysis of peat profiles in ombrotrophic bogs in Latvia. For this in-depth study of peat humification process pattern in the peat columns two ombrotrophic bogs in central part of Latvia were selected.

The results of the paleobotanical investigations (botanical composition, pollen analysis) indicate both differences and similarities of the studied bog development and peat properties. Dzelve Bog has been formed by paludification of sandy ground as a result of groundwater level increase and wet conditions in the small depression. Raised bog cotton grass peat layer covers sandy bottom, which overlays by pine-cotton grass peat. The upper part of peat section is represented by 3.2 m thick *Sphagnum fuscum* peat layer with decomposition level 9 to 17 % (Fig. 1). The development of the upper part of the bog can be explained by accumulation possibly during the Second climatic optimum. Although these bogs are located comparatively close, their local conditions for peat formation have been different.

Completely different is botanical composition of Eipurs Bog, though its origin is similar to that of Dzelve (Fig. 1). The lowest part ofEipurs is formed by fen wood-grass peat, *Hypnum* and sedge-*Hypnum* peat which is covered by transition type wood peat.bog peat of different types and decomposition degree. For example, well decomposed (40-48%) pine-cotton grass peat occurs at the depth interval of 1.18-1.39 m.

Studies of living organic material transformation (humification) is of utmost importance for better understanding of carbon biogeochemical cycling. From this perspective, the urgent character of the studies of peat properties within their profiles and identification of the links or correlations between peat age, decomposition degree, peat properties, peat botanical composition (describing and much depending on the bog development conditions, climatic and hydrological factors as well as changes of land use within the bog catchment) cannot be underestimated. On the other hand, changes of peat properties are important since they describe humification process at a molecular level and support development of new understanding of chemical and biochemical processes behind the humification.

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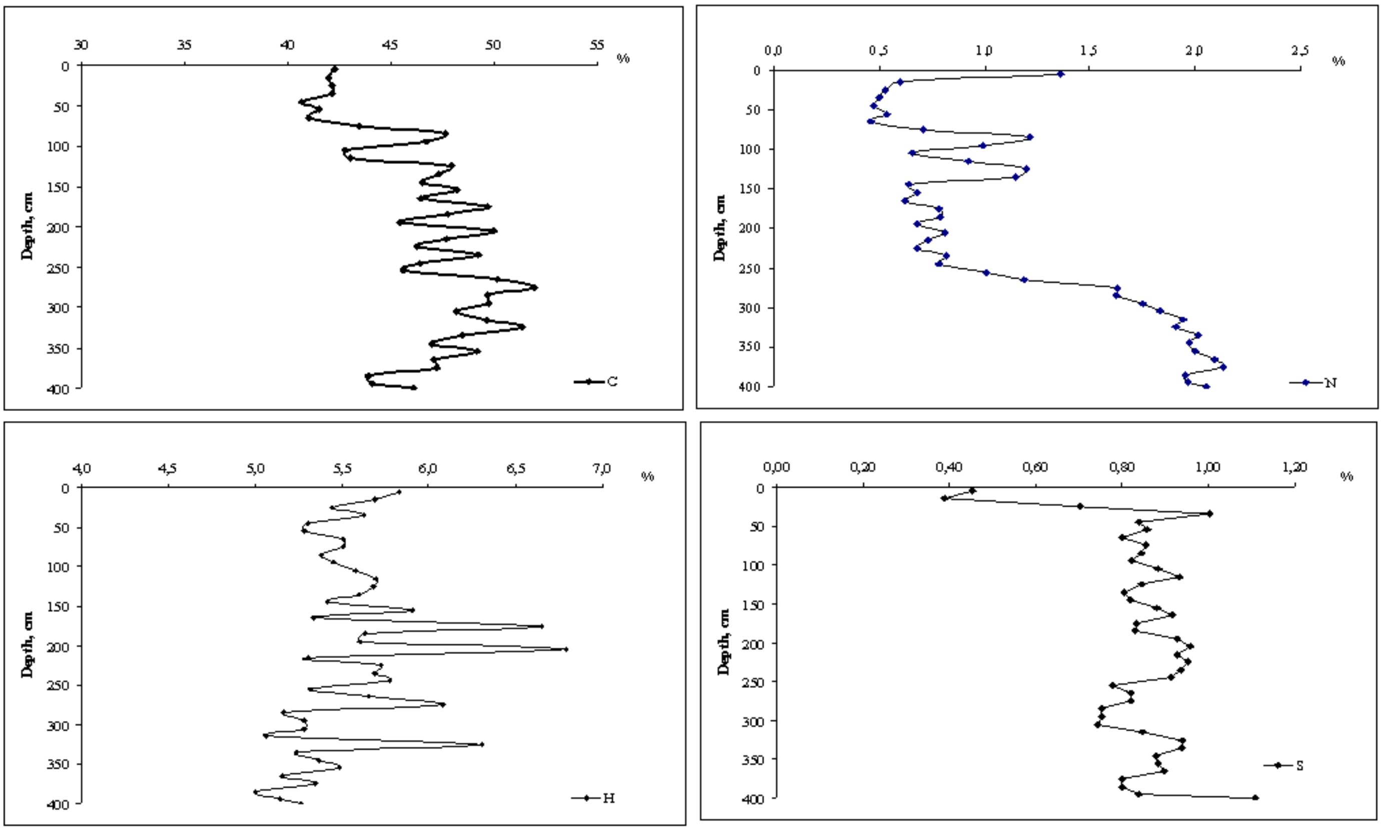

Fig.2. Elemental composition of Bog Eipurs peat

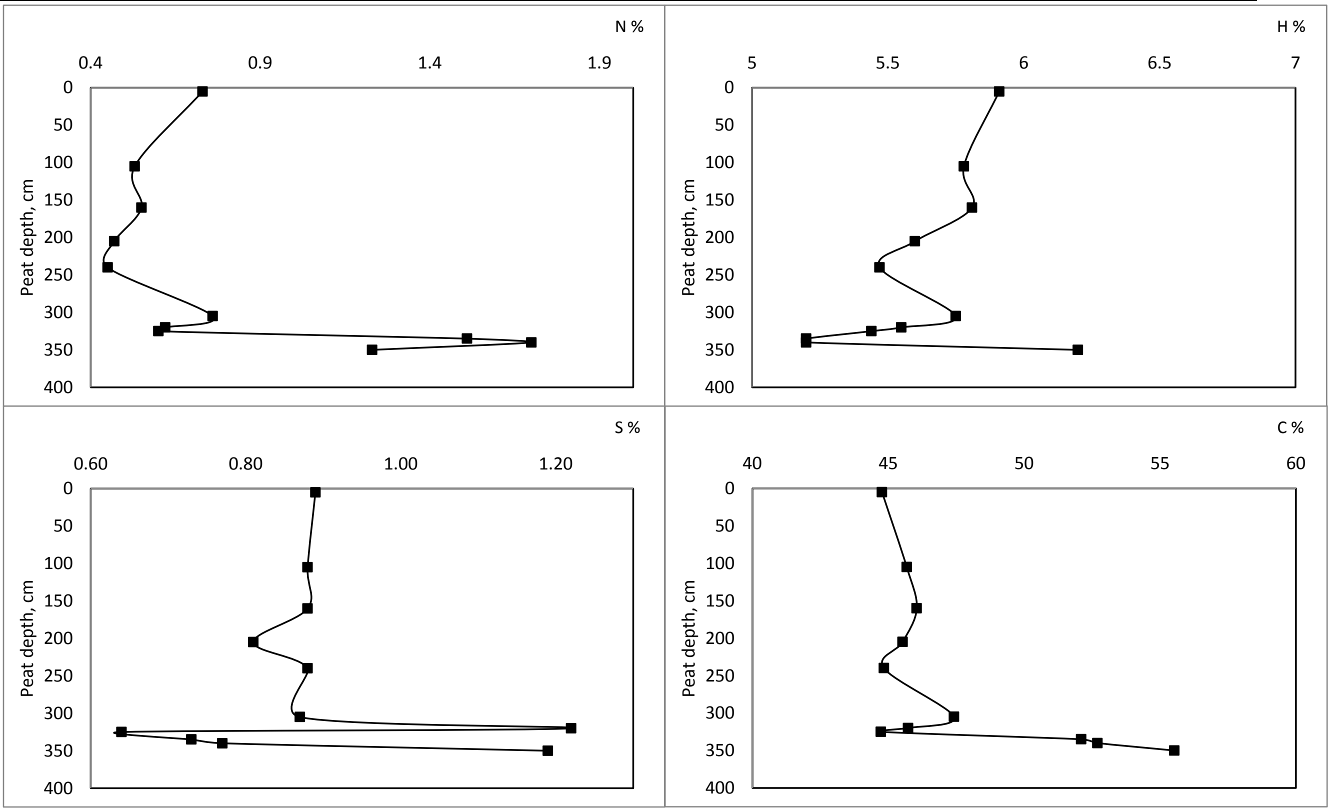

Fig.3. Elemental composition of Bog Dzelves peat

Following this approach in this study we selected two ombrotrophic bogs of similar age, located spatially close to each other (Fig. 1), yet with a highly differing peat column stratigraphy (Fig. 2, 3) and peat column botanical composition as well as decomposition degree. If the major part of the bog volume of Kroņu Dzelves bog consists of relatively homogeneous sphagnum peat with comparatively low decomposition degree, then the composition of the Eipurs bog peat is very much heterogeneous and reflect the high variability of local bog development conditions.

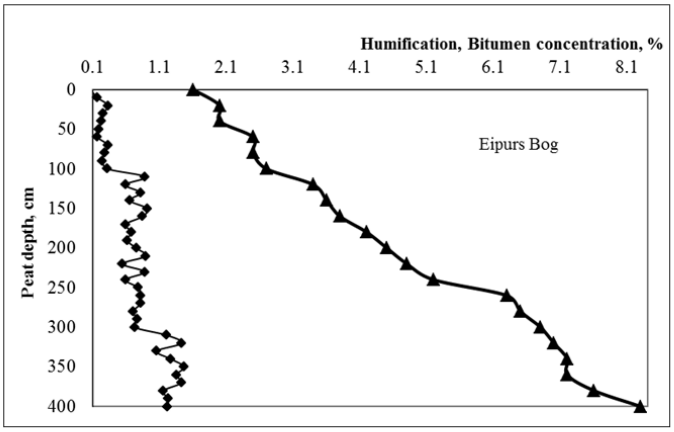

Fig.4. Humification degree and bitumen concentration in Bog Dzelves peat

Basic peat properties can be analyzed by using peat elemental (C, H, N, S) composition. The elemental composition of the studied peat cores are summarized in Fig. 2, 3. The ash contents in the studied bogs range between 0.30 ± 0.05 % and 6.10 ± 0.05 %, with the average content of 1.8 ± 0.05. Concentration of C ranges from 40 to 55 % and of H from 5.4 to 6.7 %, N from 0.5 to 1.5 %, S from 0.2 to 1.7 %, O from 38 to 49 %.

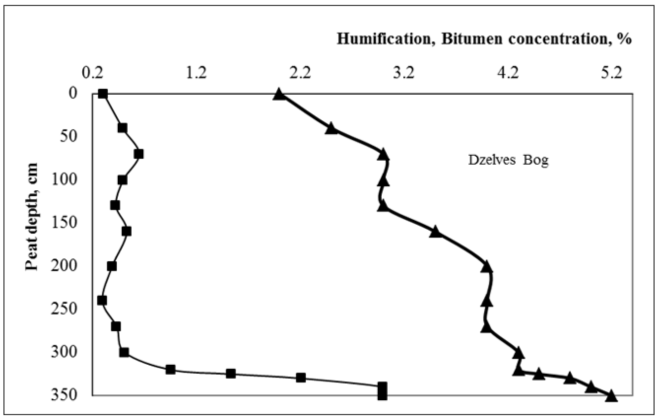

Fig.5. Humification degree and bitumen concentration in Bog Dzelves peat

The elemental composition of peat in the Eipurs bog is comparatively variable and reflects the changes in the peat decomposition degree and peat type. C concentration in the peat starts to increase at the depth 1 m up to the level of 53% and then decreases again. H concentrations demonstrate significantly higher variability, but changes of N concentrations (increase in the upper and lower horizons of the bog, but also demonstrating increased values coinciding with the

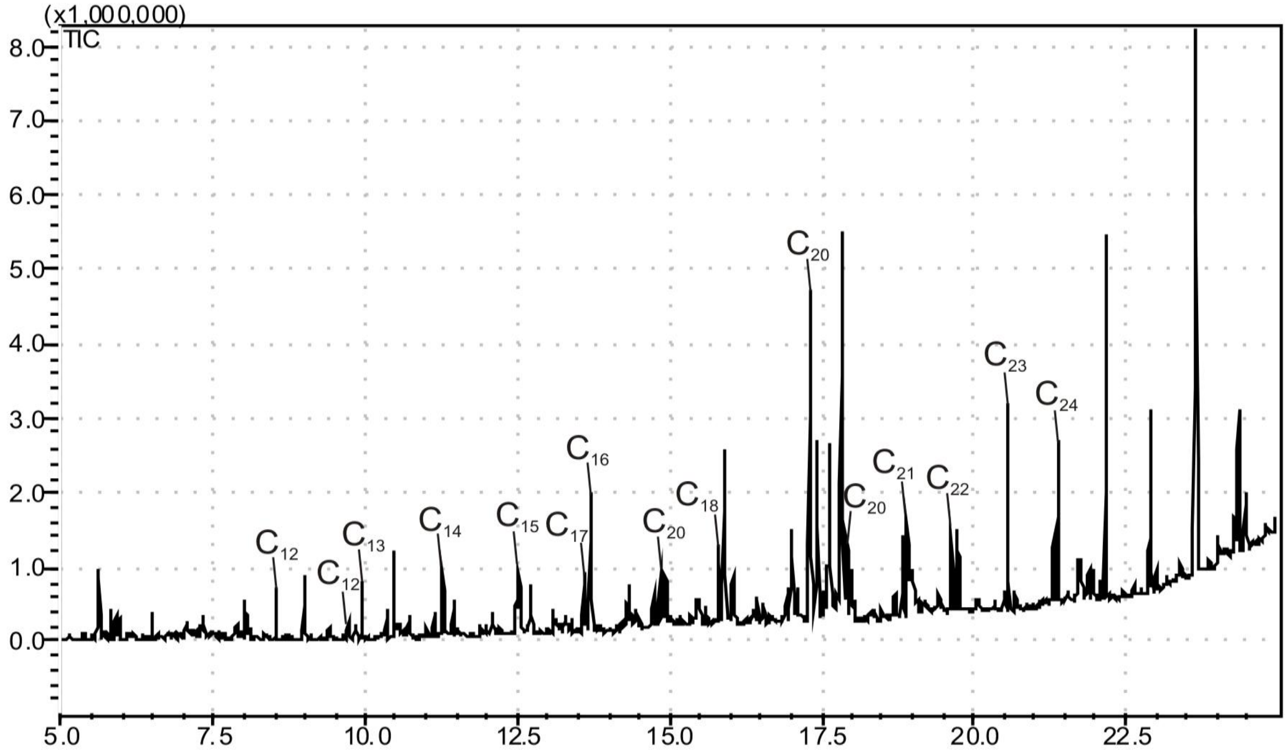

Fig.6. GC-MS chromatogram of bitumens from Bog Eipurs peat (for details see Materials and Methods)

change in the peat composition and formation conditions) could be associated with the changes in the peat botanical composition and decomposition degree. S concentrations are significantly lower just in a few upper centimeters of the peat bog, but comparatively stable along the peat column. At the same time, the elemental composition (Fig 3) of Dzelves bog is very much different and largely reflects the peat column composition: the C content in the upper layers is much lower (~ 45 %) and comparatively uniform down to depth of 3.25 m, but then rapidly increases reaching 55 % for highly decomposed peat.

Total bitumen amount in peat composition reflects the degree of transformation of lipids and development at first of hydrocarbon structures. The total amount of bitumens found in the studied bogs ranges from 1 % till 8 % and is higher in peat with a higher decomposition degree in Bog Eipurs (Fig. 4, 5).

The values of the bitumen concentrations are in the range common for raised bogs with the medium – high peat decomposition degree [1].

However, some notable distinctions between humification indicators (humification degree) and bitumen content can be found: if the pattern of changes of humification degree can be related to peat decomposition degree and is highly variable within the peat profile, then bitumen concentration is relatively evenly increasing with bog depth.

Thus a notable difference between the peat humification processes and genesis of hydrocarbons can be stated – indicating evidently different mechanisms governing the transformation processes of organic matter and genesis of thermodynamically more stable (than such ingredients of peat as carbohydrates etc.) structures.

GC-MS of peat bitumens reveal presence of the wide range of both aromatic and aliphatic hydrocarbons with odd and even carbon number ranging from C_{12} to C_{27} Also polynuclear aromatic hydrocarbons were found, however in much less amounts than those of aliphatic hydrocarbons. GC-MS analysis indicated the presence of pyrene (M^+ 202), Benzo(a)anthracene (M^+ 228), benzo(b)fluoranthene and perylene (M^+ 252).

IV. Conclusions

The total amount of bitumens found in the studied bogs ranges from 1.5 % till 8 % and thus is within the range common for raised bogs. The amount of bitumens is higher in peat with a higher decomposition degree. However notable differences between humification indicators (humification degree) and bitumen content can be found: if the pattern of changes of humification degree can be related to peat decomposition degree and is highly variable within the peat profile, then bitumen concentration is relatively evenly increasing with bog depth. GC-MS analysis proved presence of a number of aliphatic and aromatic hydrocarbons present in peat bitumen.

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Laura Kļaviņa, Pēteris Mekšs, Inese Silamiķele. Kūdras bitumenu sastāvā ietilpstošo ogļūdeņražu analīze augsto purvu profilos
Bitumeni ir nozīmīgs kūdras ingredients. Bitumi kūdras sastāvā veidojas, pārveidojoties kūdru veidojošo augu sastāvā ietilpstošajiem hidrofobajiem savienojumiem, kā arī kūdras sastāvā ietilpstošo mikororganismu metabolītu pārvērtību procesā. Bitumenu sastāvā ietilpst vaski, steroīdu atvasinājumi un ogļūdeņraži, kas ir uzskatāmi par minēto hidrofobo savienojumu pārvērtību galaproduktiem. Ir pamats uzskatīt, ka ogļūdeņražu veidošanās (kas neietilpst dzīvo kūdru veidojošo augu sastāvā) ir uzskatāma par nozīmīgu procesu, kas modelē fosilā kurināmā veidošanos. Pētījumā analizēts bitumenu sastāvs kūdrā un to mainības raksturs divos atšķirīga sastāva augstā tipa purvos. Veikta purvu kūdras sadalīšanās pakāpes, botāniskā sastāva analīze, raksturota kūdras humifikācijas pakāpe un noteikts elementsastāvs un kūdras vecums, izmantojot ^{14}C datēšanu. Noteikto kūdras sastāva mainības rādītāju ievērojamās atšķirības uzrāda būtisko dažādību kūdras veidošanās procesos, kas tajā pat laikā pamato izvēlēto purvu izpētes izmantošanu, lai raksturotu vides faktoru ietekmi uz kūdras sastāvu. Pierādīts, ka bitumenu sastāva un kūdras humifikācijas pakāpes mainības raksturs būtiski atšķiras atkarībā no kūdras sastāva un to veidojošo augu uzbūves, un līdz ar to acīmredzami arī procesu raksturs, kas kontrolē to mainību. Bitumenu koncentrācijas atrodas intervālā, kas raksturīgs augstā tipa purvu kūdrai, bet bitumenu sastāvā ietilpst ogļūdeņraži ar oglekļa atomu skaitu no C_{12} līdz C_{27}, turklāt to skaitā ietilpst gan lineāras uzbūves, gan aromātiskie ogļūdeņraži. Pētījuma turpinājumā paredzēts veikt konstatēto ingredientu kvantificēšanu, kā arī raksturot kūdras vasku un sveķu sastāvu.

Лаура Клявиня, Петерис Мэкш, Инесе Силамикеле. Анализ углеводородов в составе битуменов торфа
Исследован состав битумов и их изменения в профилях торфа двух верховых болот. Результаты показали, что исследованные битумы состоят из углеводородных соединений как циклического, так и алифатического строения, с количеством атомов углерода от C_{12} до C_{27}**.** Характер изменений состава битумов в обоих случаях существенно отличается от характера изменения степени гумификации. Очевидно что природа процессов, связанных с этими изменениями, также различна. Констатированные концентрации битумов типичны для верхового торфа.
Битумы являются существенным ингредиентом торфа. Битумы состоят из восков, производных стеринов, углеводородов и других компонентов, которые при малой степени разложения близки по составу к липидам растений-торфообразователей. Есть основание считать, что образование углеводородов (которые не включают торфообразущие живые растения), можно рассматривать как процесс моделирования образования горючего ископаемого материала. Определена степень разложения торфа, анализ ботанического состава, охарактеризована степень гуминификации и определён элементный состав и возраст торфа, используя углеродное датирование ^{14}C. Определенные показатели изменчивости торфяного состава указывают на значительную разновидность процессов образования торфа, и в то же время выбранные болота показывают влияние факторов среды на процесс торфообразования.
В продолжении исследования предусматривается количественная оценка уже определенных ингредиентов, и также охарактеризован состав воска и смолы торфа**.**